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MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO) 28 Feb 2003

Capt. Gonzalez
[redacted]

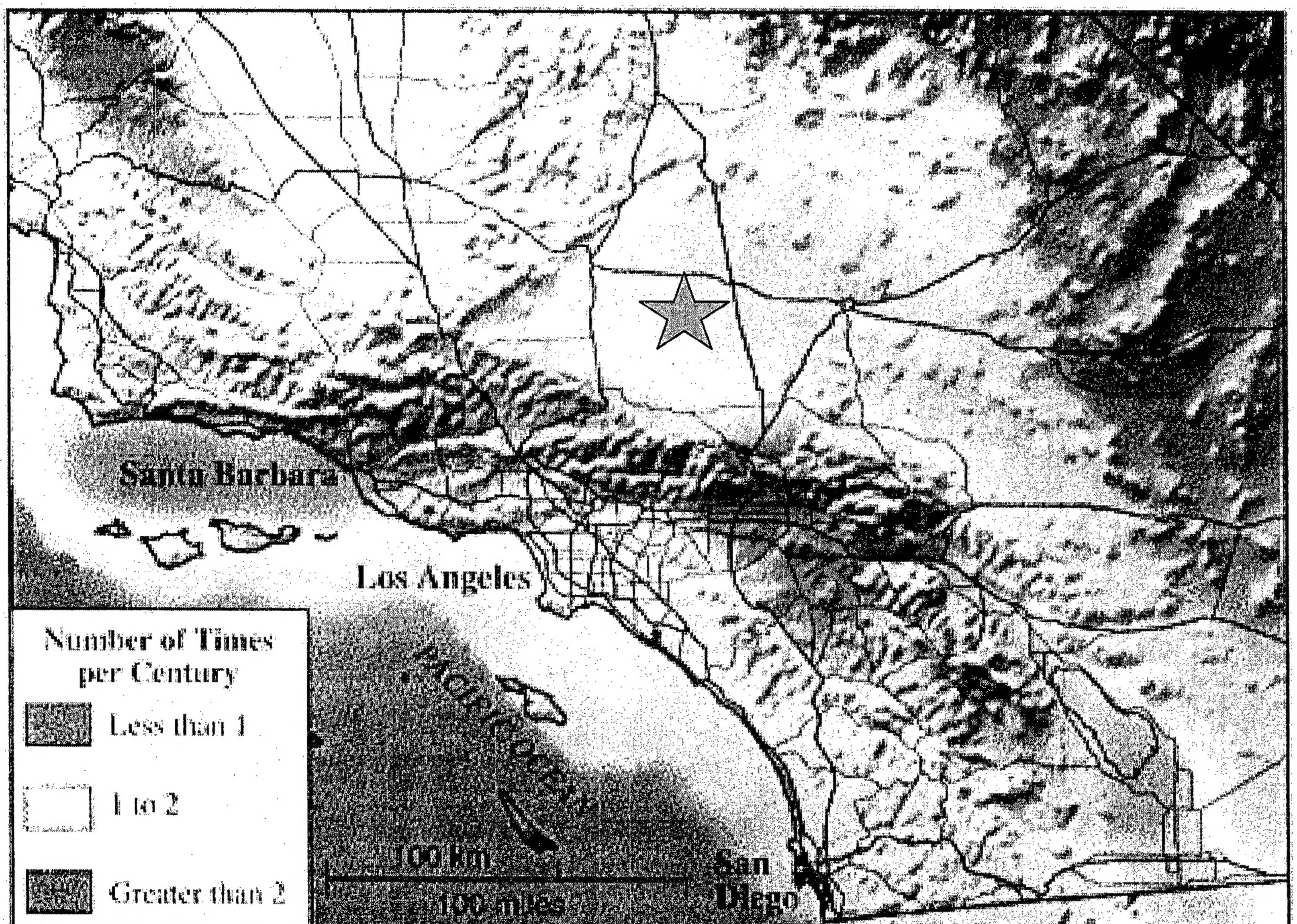
SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-047**
Timothy S. Haddad; Brian Moore; Capt. Rene Gonzalez, "POSS Polystyrene Copolymers, Reactivity Ratios and Control"

American Chemical Society Conference **(Statement A)**
(New Orleans, LA, 23-27 Mar 2003) **<u>(Deadline: 21 Mar 2003)</u>**

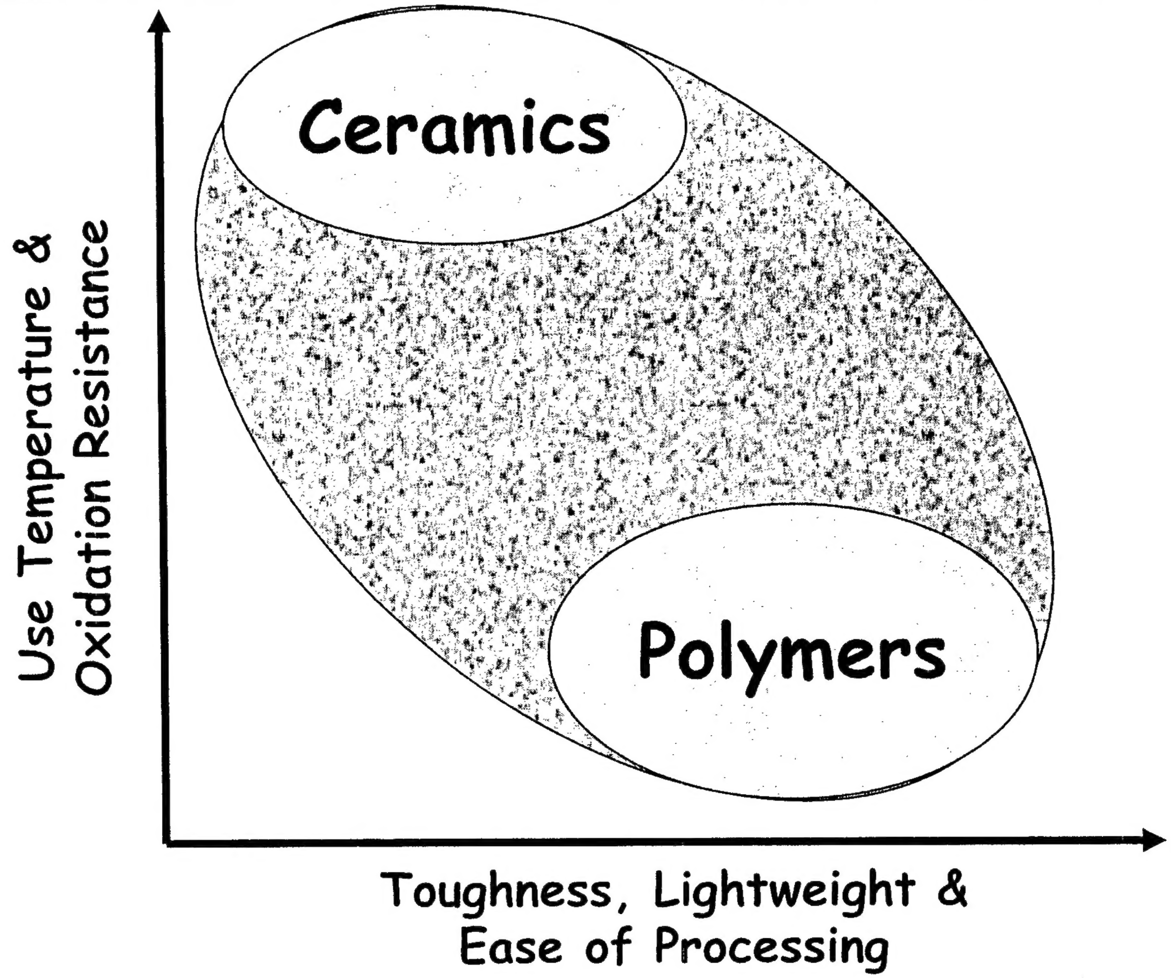
POSS POLYSTYRENE COPOLYMERS REACTIVITY AND CONTROL

Brian Moore, Tim Haddad
and Rene Gonzalez
Erc Inc., Air Force Research Lab

Edwards Air Force Base

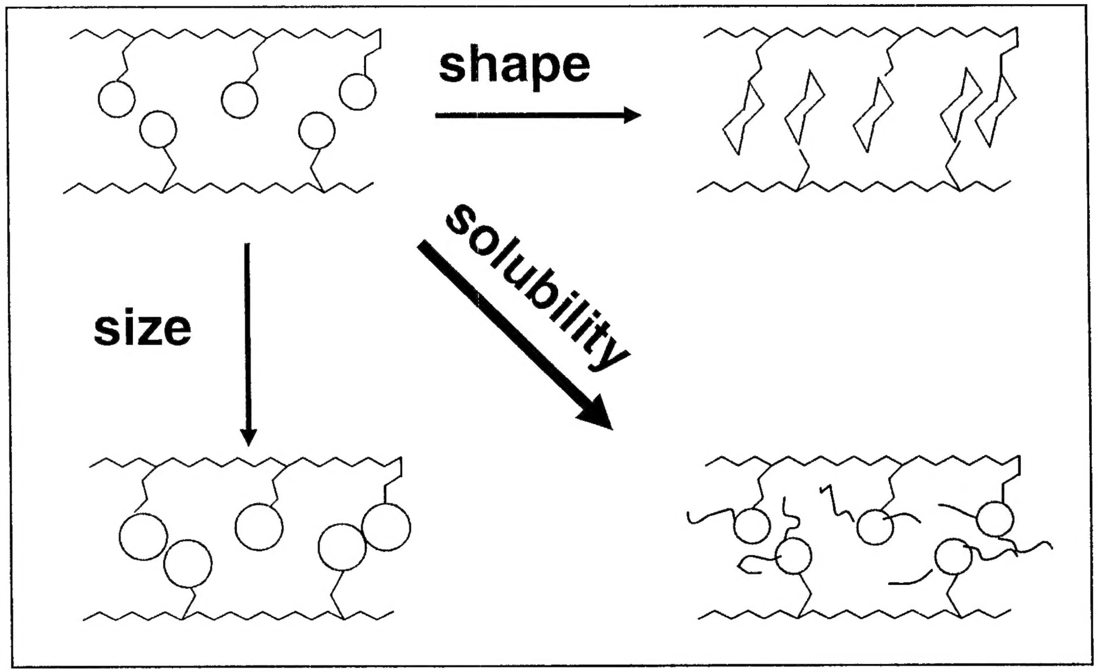


Hybrid Inorganic/Organic Polymers



- Hybrid plastics bridge the differences between ceramics and polymers

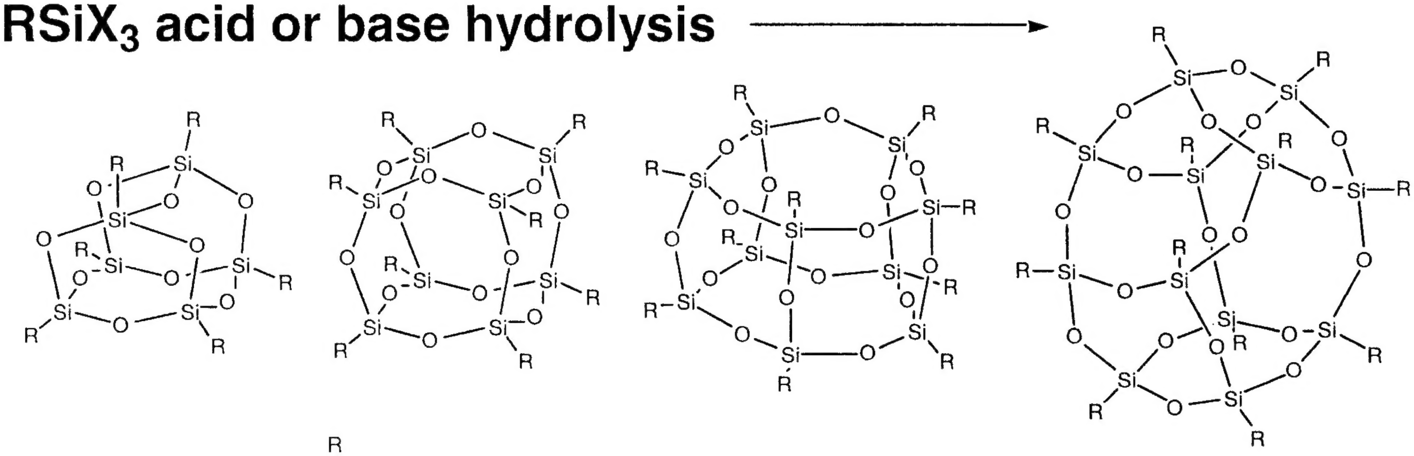
Structure-Property Relationships

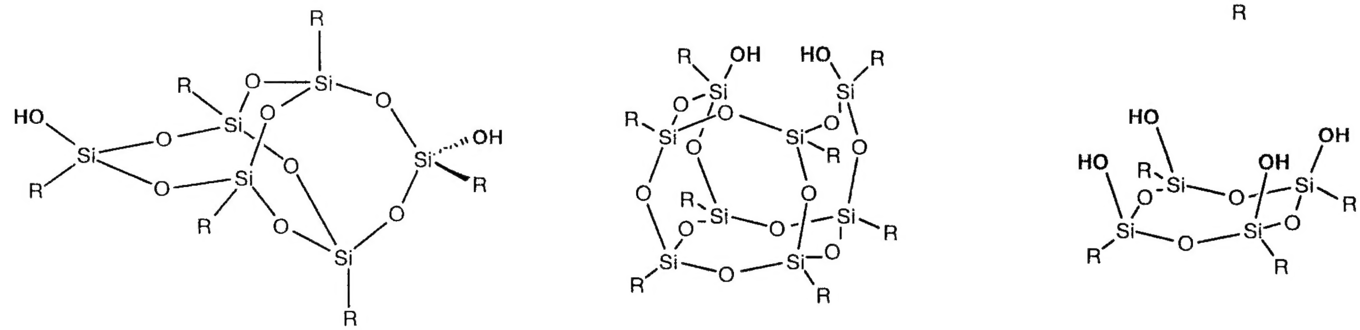


- Maximizing property enhancements through changes at the nano level
- Polymer miscibility vs. POSS/POSS interactions
- Molecular Weight Dependence on Mechanical Properties

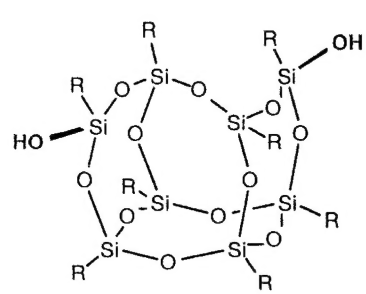
POSS Synthesis

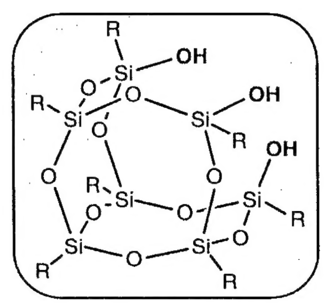
$RSiX_3$ acid or base hydrolysis ⟶



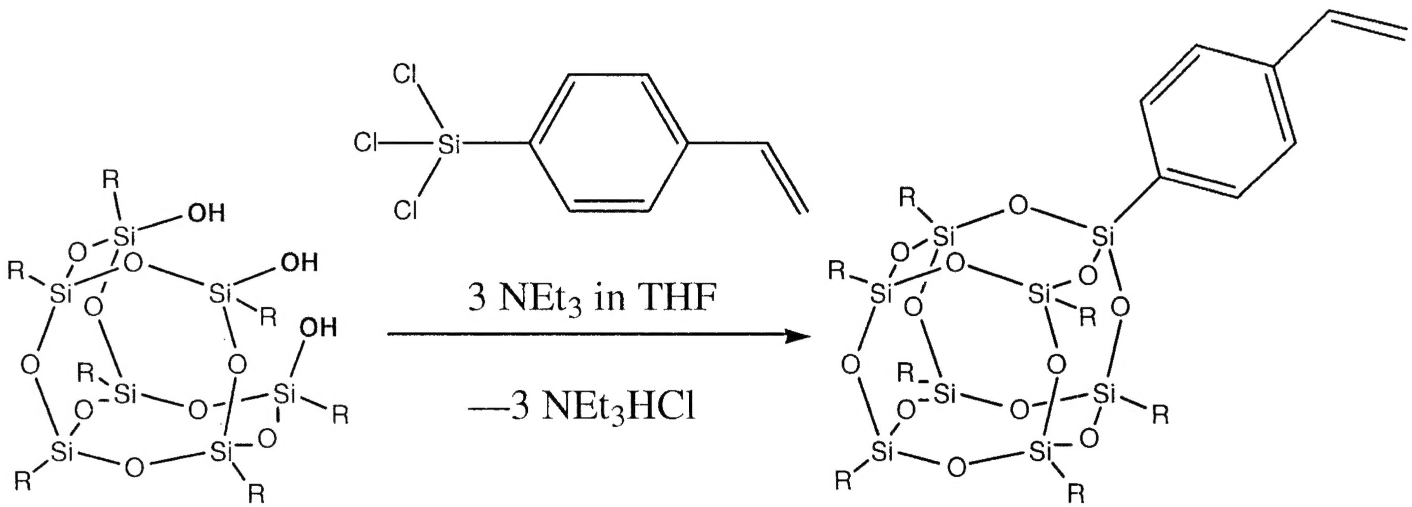


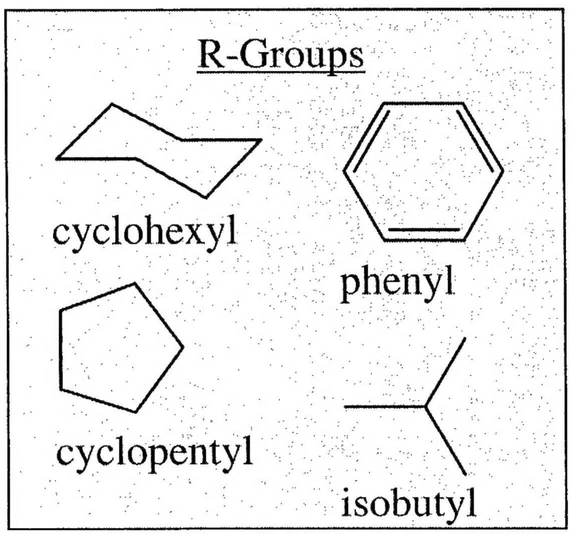
Brown & Vogt: JACS, 1965, 4313
Feher et al: JACS, 1989, 1741;
Organometallics, 1991, 2526;
Chem Comm, 1999, 1705, 2309





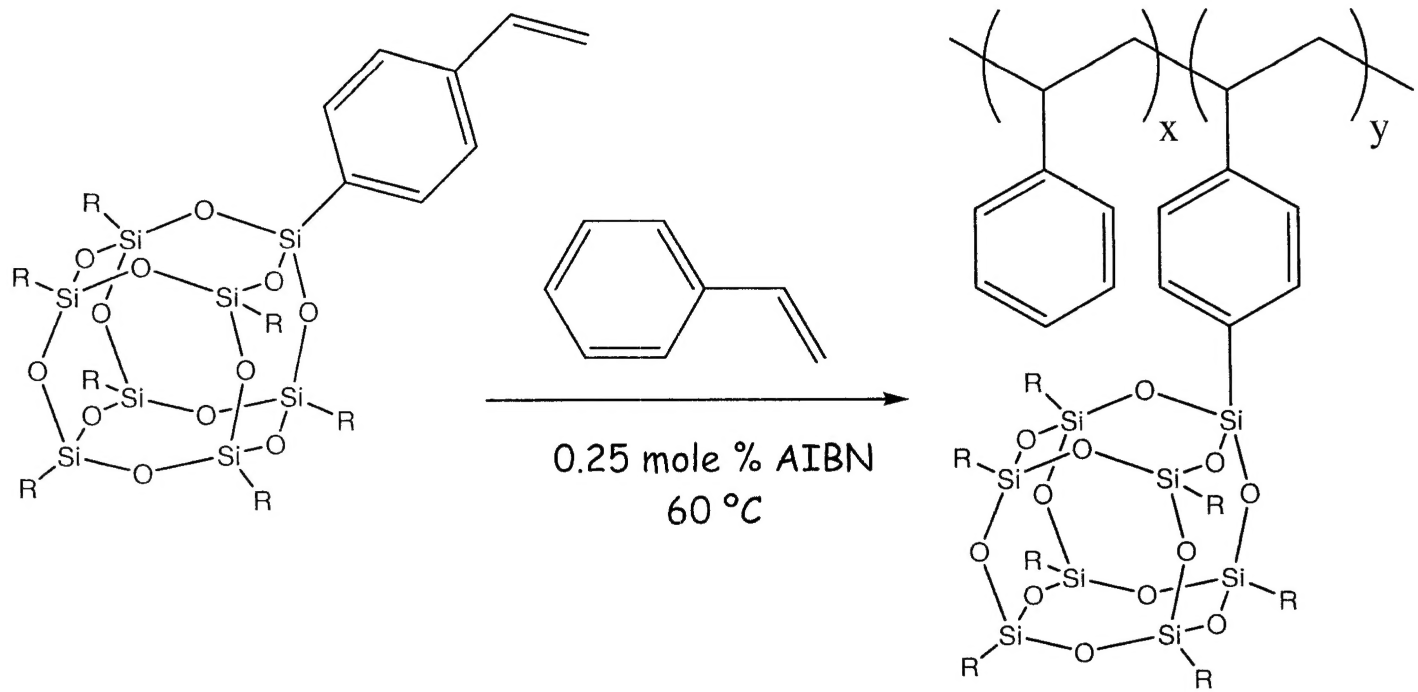
POSS-Styrene Monomer Synthesis





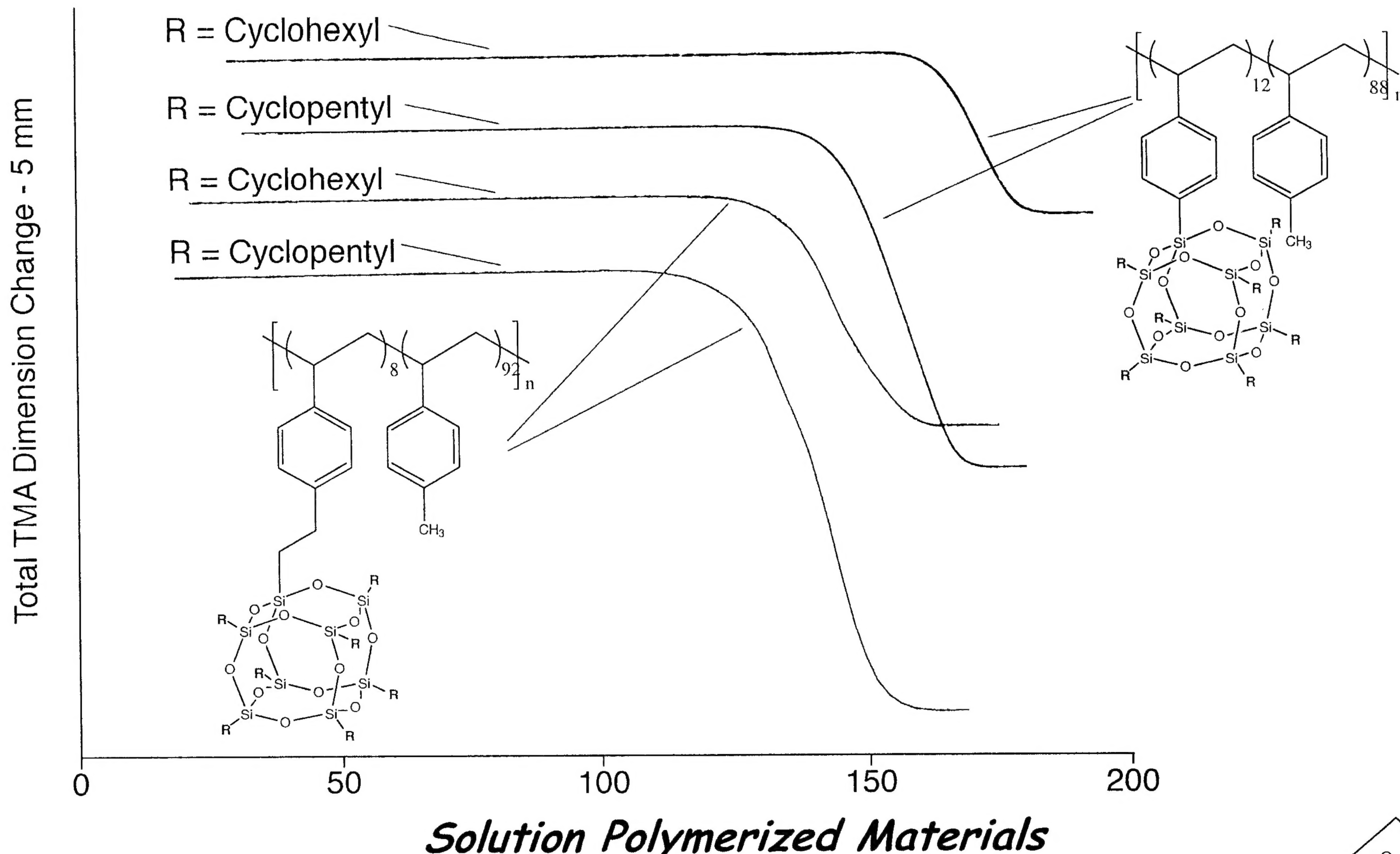
- High-yield syntheses
- Phenyl derivative requires inverse addition
- J. Inorg. Organomet. Polym., Vol 11, 2002, p. 155

POSS-Styrene Copolymer Synthesis

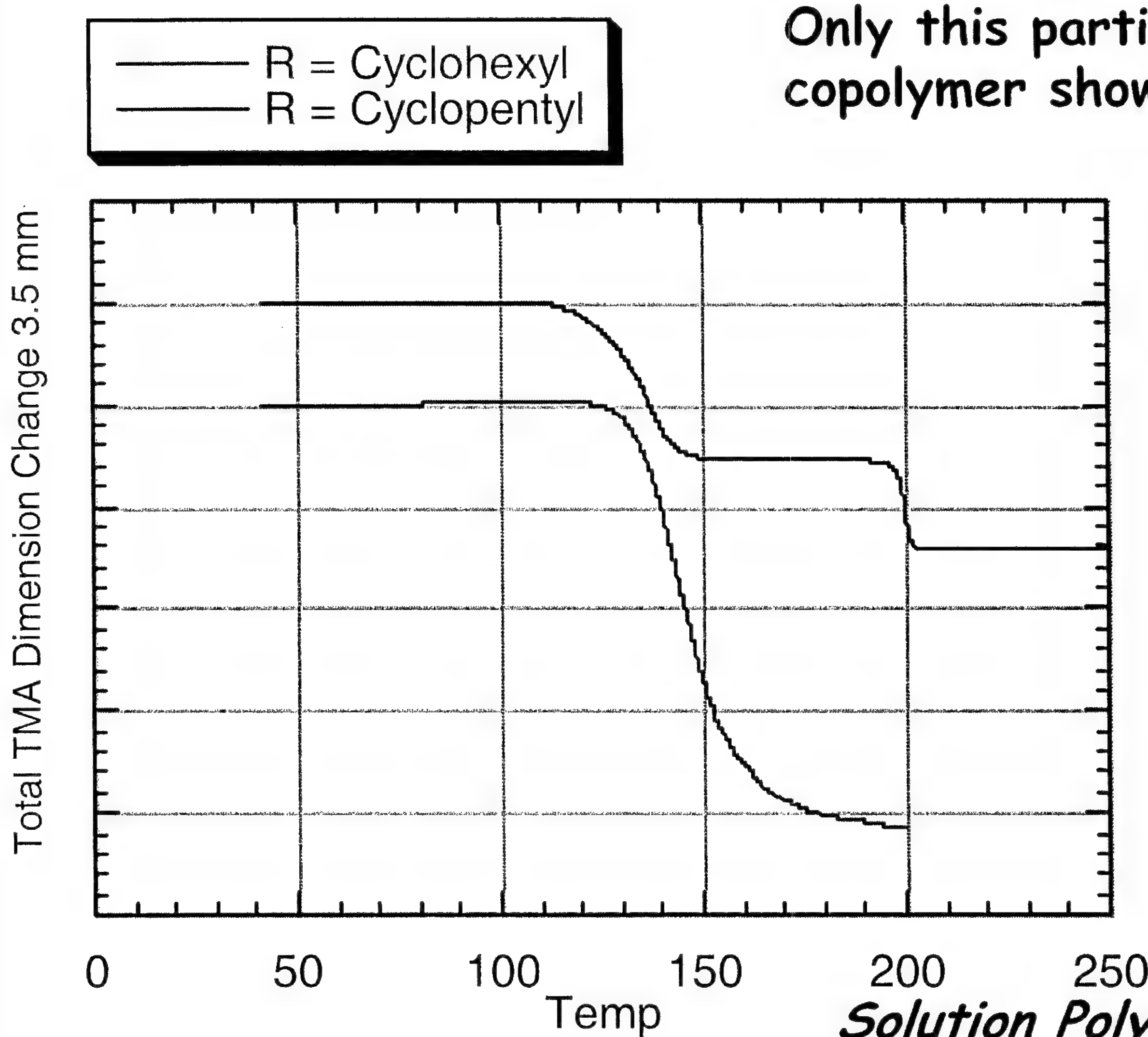


- Solution polymerization in toluene or bulk polymerization possible
- Polymerization is limited by solubility of the POSS-macromer
- Isobutyl-POSS is the most soluble, Phenyl-POSS the least soluble
- Macromolecules Vol. 29, 1996 p. 7302

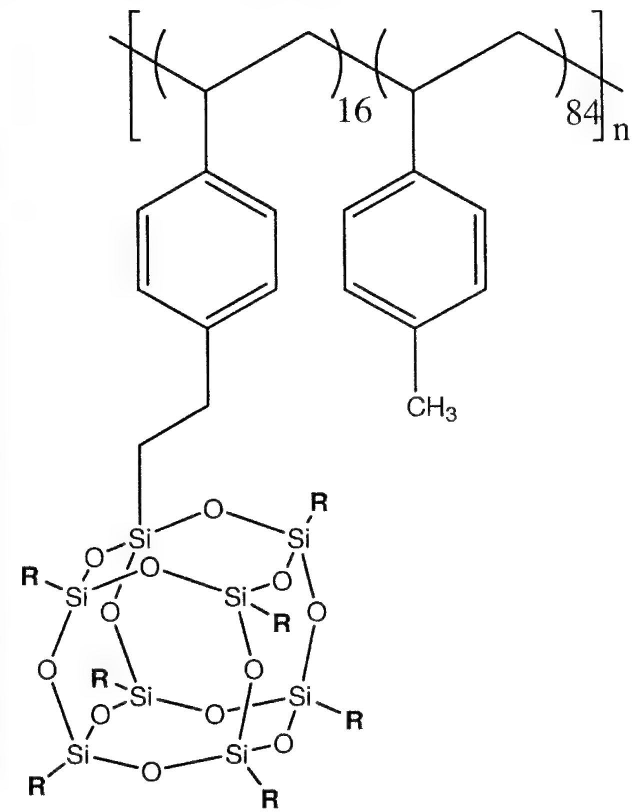
TMA Comparison: POSS Group Effect



TMA Evidence for a Blocky Copolymer



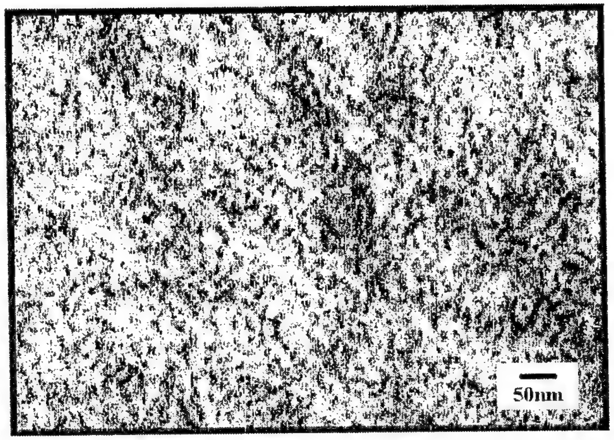
Only this particular cyclopentylPOSS copolymer shows two transitions.



Solution Polymerized Materials

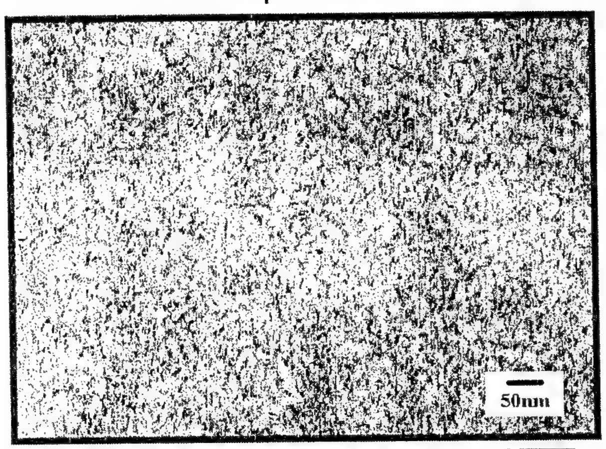
TEM Comparison of POSS Norbornenes vs Styrene

50CyPOSS/PN



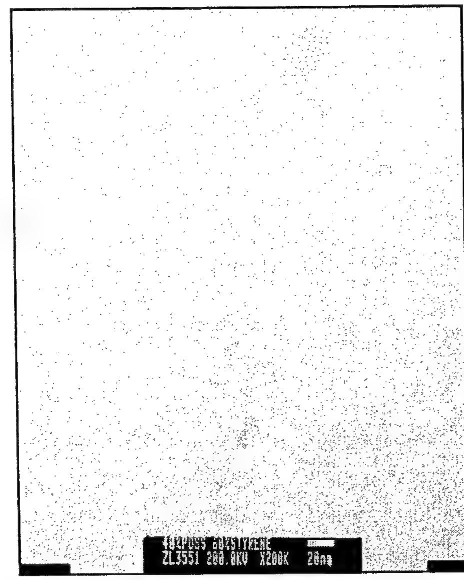
"Coarse" Cylinder Nanostructure
(Diameter ~ 12nm)

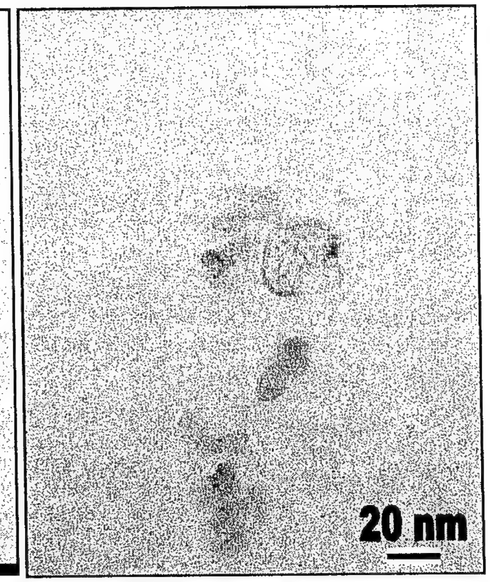
50CpPOSS/PN



"Fine" Cylinder Nanostructure
(Diameter ~ 6nm)

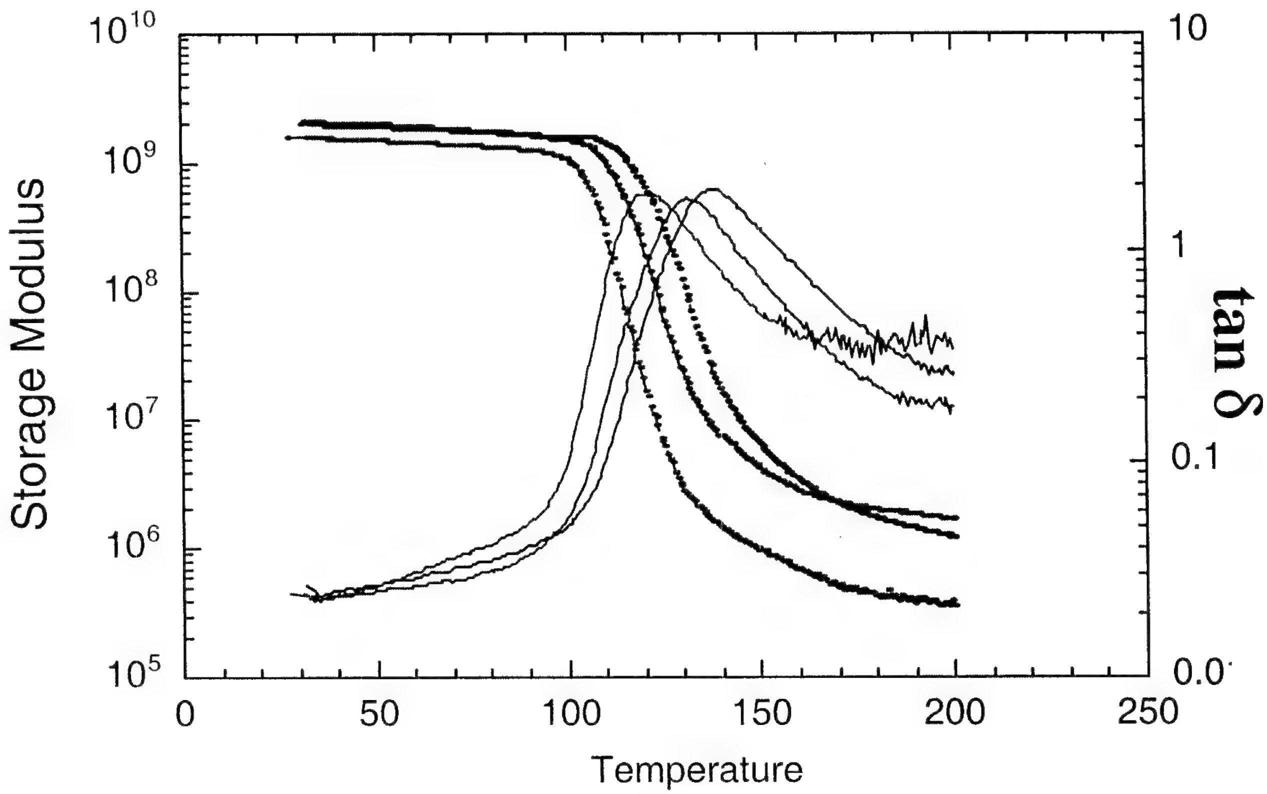
40% isoButylPOSS polystyrene

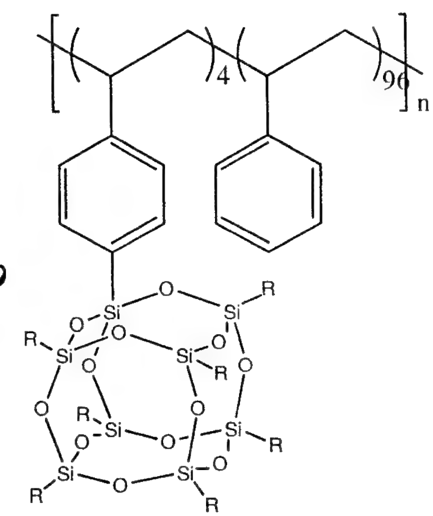




Random copolymers of cyclohexyl and cyclopentyl POSS norbornenes form a nanocomposite imaged by TEM. A random copolymer of isobutylPOSS-styrene shows no structure and complete dispersion of the POSS in the copolymer is assumed.

DMA of 30 Wt. % POSS-Polystyrenes

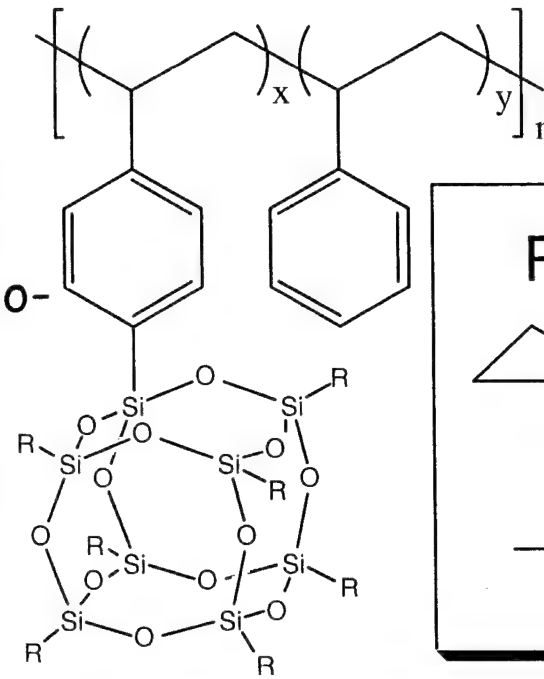


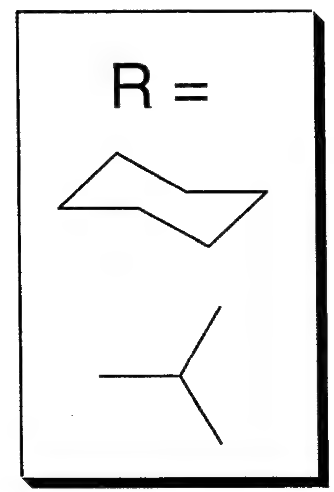


- Comparison of isobutyl, cyclopentyl & cyclohexyl
- High Molecular Weight Bulk polymerized samples

Solubility of High Molecular Weight Copolymers

Both bulk and solution polymerization methods were used to find that highly entangled POSS-polystyrene can form an insoluble gel. If the R-group is cyclohexyl, then this gel effect occurs at very low POSS content. Much higher loadings of isoButylPOSS are required to obtain similar insoluble materials.





POSS-POSS Interactions can Dominate to form insoluble "Gels"

POSS type	Degree of polymerization	Wt% POSS	Styrene/POSS
Cyclohexyl	> 3000	5-10	~150:1
isoButyl	~4000	35-40	~17:1

Reactivity Ratios for Styrene / POSS-Styrene

M_1: Styrene Monomer

M_2: POSS-Styrene Monomer

M_1^*: growing polymer M_1-radical

M_2^*: growing polymer M_2-radical

r_1: reactivity ratio for Styrene

r_2: reactivity ratio for POSS-Styrene

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$$

$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$$

$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$$

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

The composition of a copolymer cannot be determined by the homopolymerization rates of the two monomers.

Assume the chemical reactivity of the propagating chain in a copolymerization to be dependent on the monomer at the growing end.

Reactivity Ratios for Styrene / POSS-Styrene

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Alternating Copolymerization: $r_1 = r_2 = 0$

Block Copolymerization: $r_1 > 1$, $r_2 > 1$

Random Copolymerization: $r_1 r_2 = 1$

Reactivity Ratios calculated using the copolymer composition equation:

$$F1 = \frac{(r_1 f_1 f_1 + f_1 f_2)}{(r_1 f_1 f_1 + 2 f_1 f_2 + r_2 f_2 f_2)}$$

r_1 = reactivity ratio for styrene
r_2 = reactivity ratio for POSS-styrene
F_1 = mole fraction of styrene in copolymer
f_1 = mole fraction of styrene monomer in feed
f_2 = mole fraction of POSS monomer in feed

Reactivity Ratios: Challenges

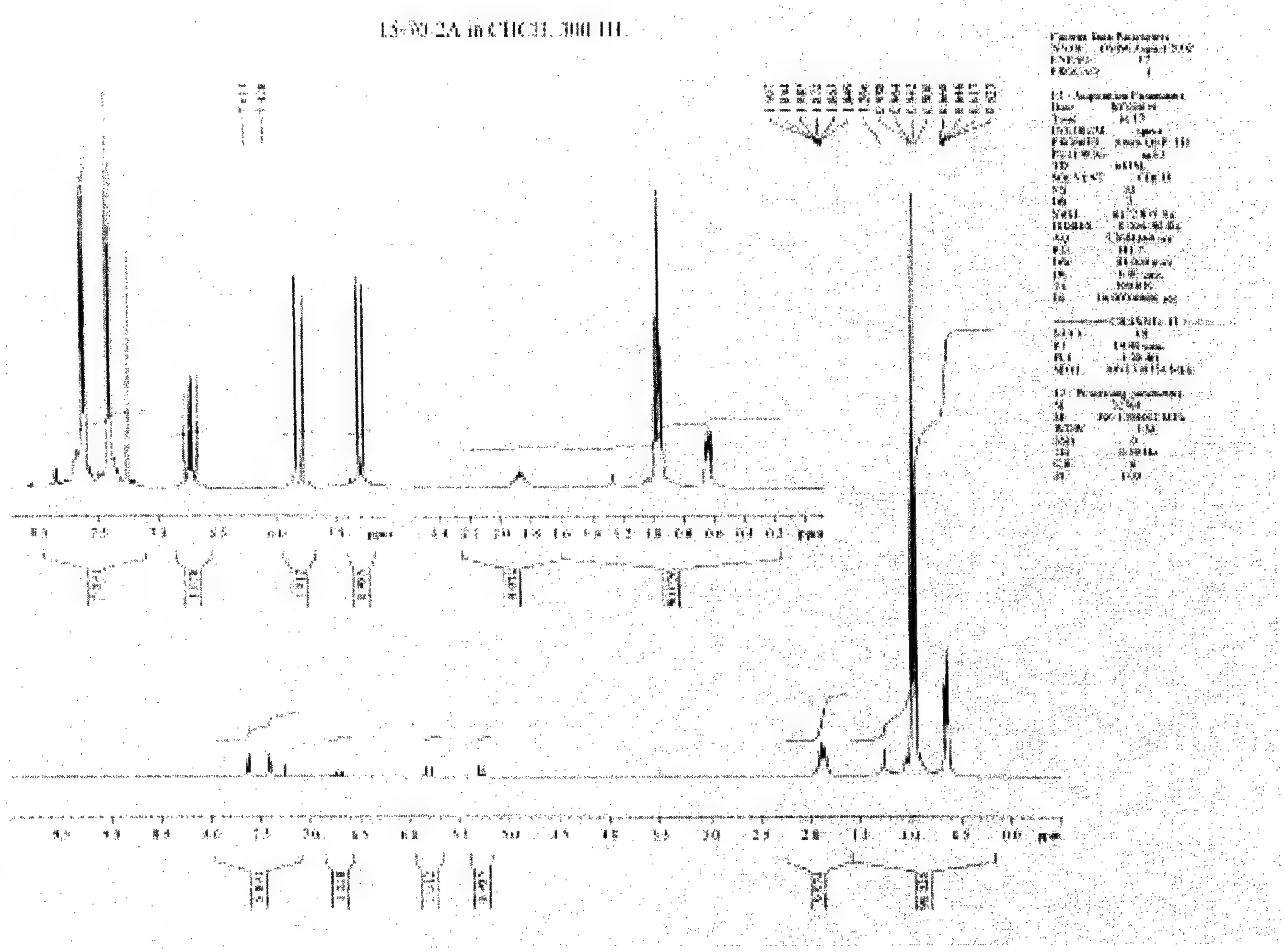
- Polymerizations <u>must</u> be carried out to only 3-5% completion.
  -Reactions were run for 3 hours and monitored by ^{1}H NMR.

- The small amount of polymer formed (a solid) must be separated from a large amount of unreacted POSS-monomer (also a solid).
  -Achieved with precipitation of polymer using Ether/MeOH

- Accurately determine the amount of POSS in each copolymer.
  -IR analysis coupled with NMR integrations.

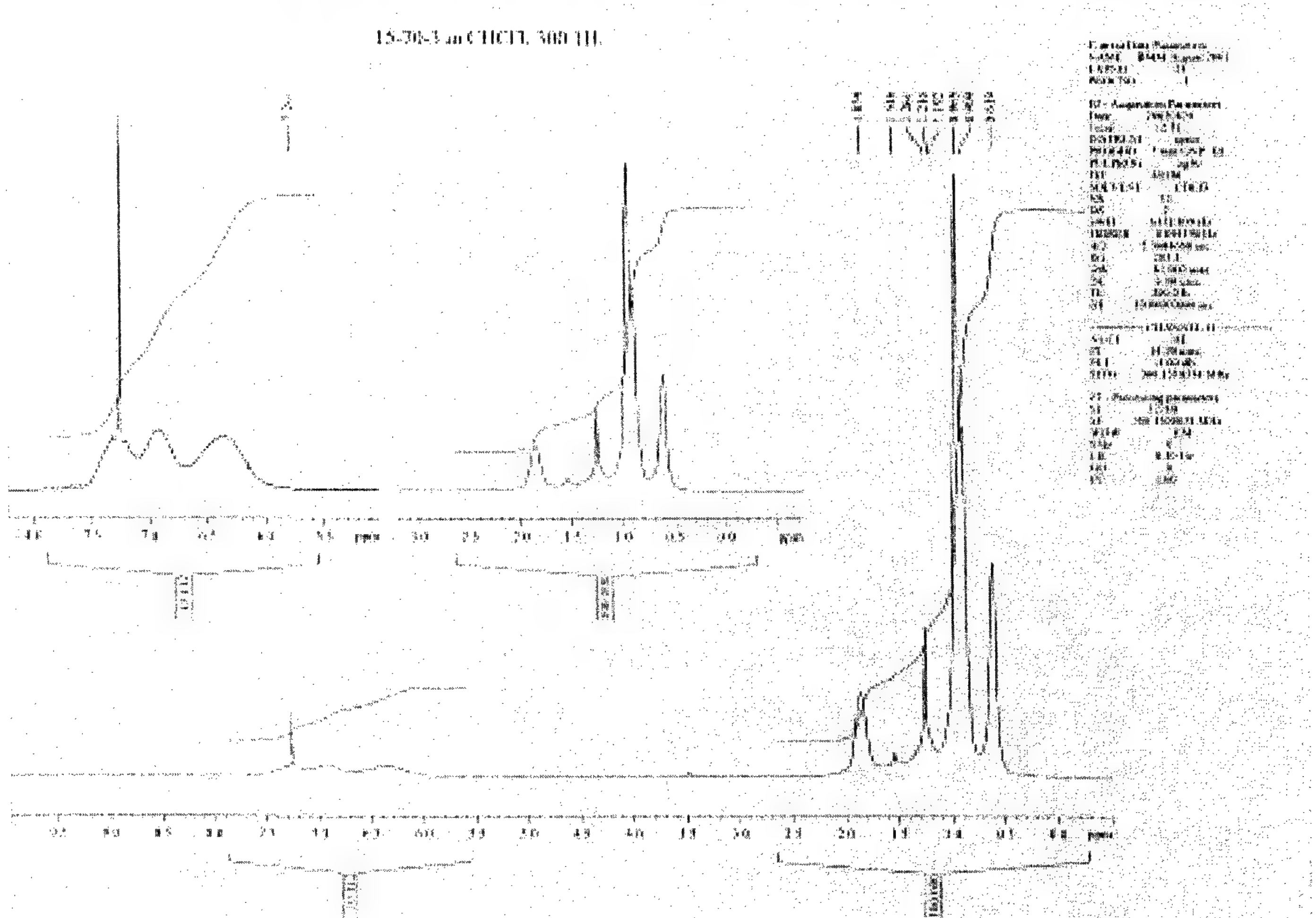
- Carry out a full (10-90) range of mole % POSS reactions while maintaining the same concentration of monomers and initiator.
  -Achieved best with isoButylPOSS as it has favorable solubility.

NMR Spectra of Crude Reaction Product



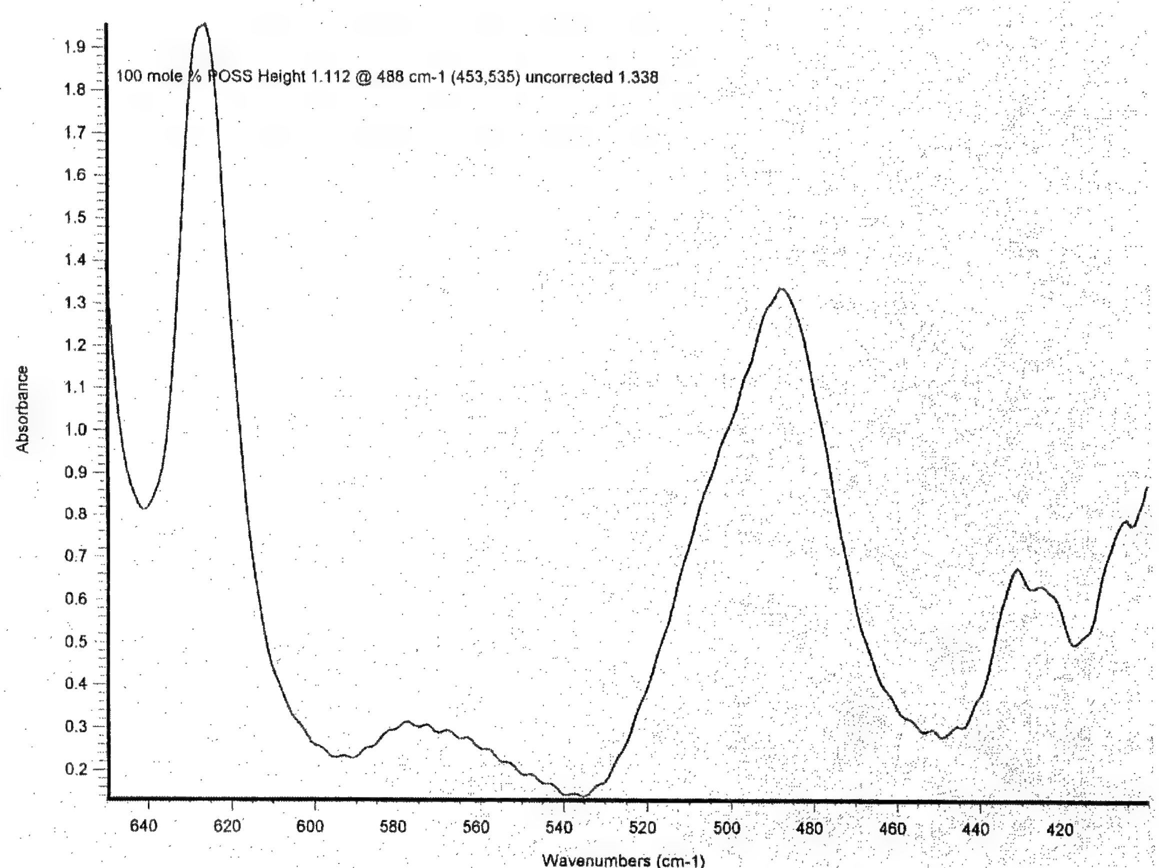
This spectrum shows mostly POSS-monomer with some copolymer

NMR Spectra of Isolated Copolymer



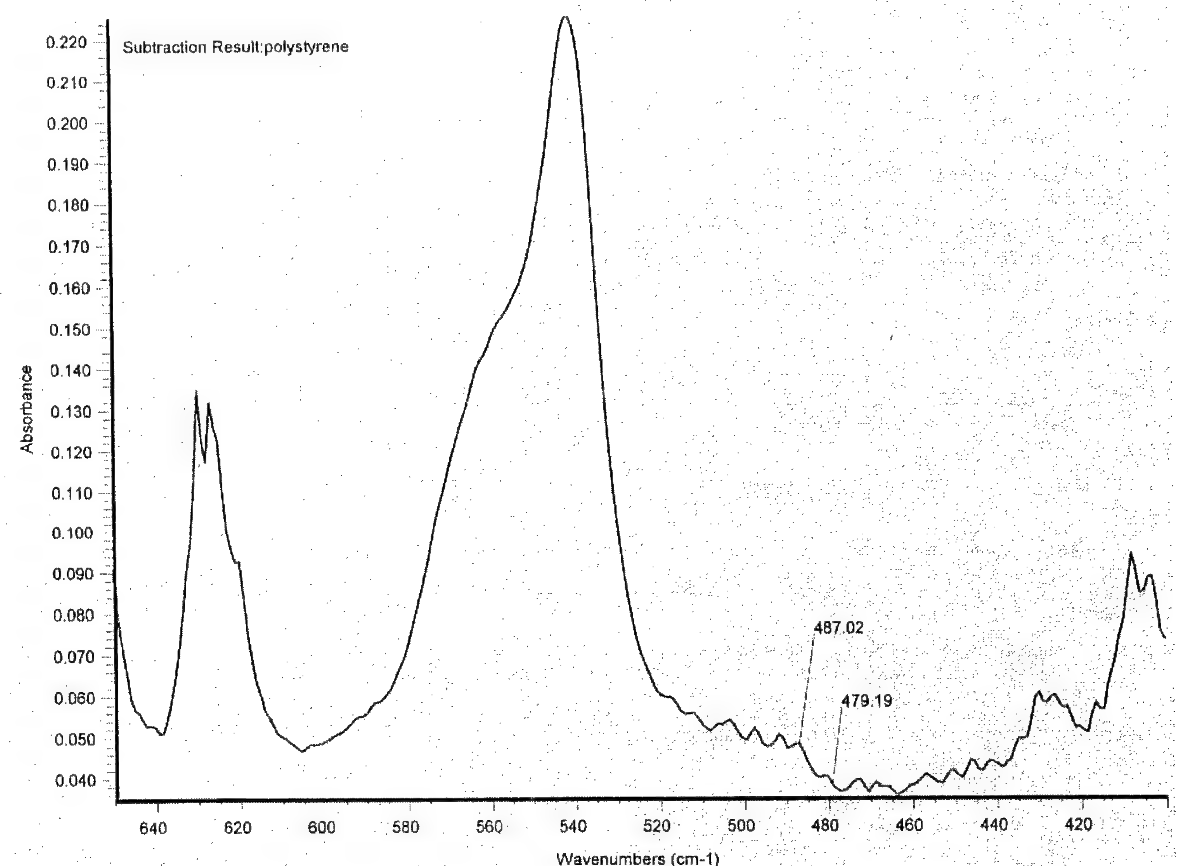
This spectrum shows monomer-free copolymer

Infrared Spectrum of POSS-Styrene



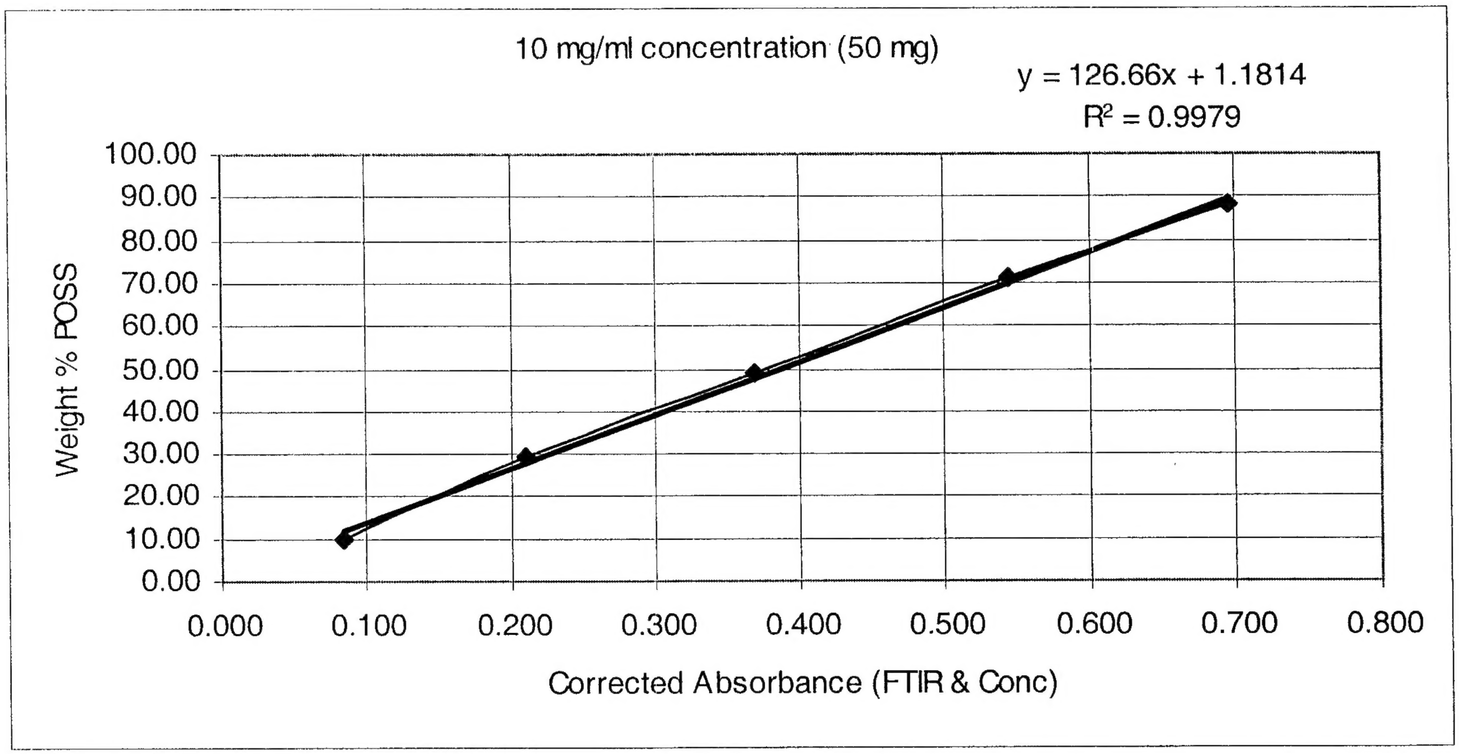
An iButyl POSS-Styrene cage has a Si-O stretch at 483 cm-1

Infrared Spectrum of Polystyrene



Polystyrene has no absorbance at 483 cm^{-1}

IR Calibration Curve for POSS Standards



Reactivity Ratio For POSS-Styrene

Data by FTIR
r_1 Styrene = 1.19
r_2 POSS-Styrene = 0.17

These reactivity ratios were determined by analysis of seven polymerizations, which yielded 21 pairs of equations and the two variables (r_1 and r_2)

Data by ^1H NMR
r_1 Styrene = 1.09
r_2 POSS-Styrene = 0.34

SUMMARY

Nano-sized inorganic clusters (POSS) can be incorporated into polystyrene copolymers from 1-99 wt %.

These POSS clusters cause increases to the thermal transitions and mechanical properties of the polymers they are copolymerized into.

The POSS effect on the properties of analogous polymers shows a dependency on the type of alkyl group on the POSS cluster.

A degree of control over molecular weight can be made using standard kinetic polystyrene parameters. High molecular weight is necessary to maintain good mechanical properties.

Reactivty ratios show that styrene monomer has no preference for reaction with itself or with a POSS-styrene. A POSS-styrene monomer, however, is more likely to react with styrene than with itself. Therefore, a copolymer sequence should be close to random.

Acknowledgement$

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